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Summary

Silicon carbide (SiC) and Si₃N₄ materials were tested in various turbine engine combustion environments chosen to represent either conventional fuel-lean or fuel-rich mixtures proposed for high-speed aircraft. Representative chemical vapor-deposited (CVD), sintered, and composite materials were evaluated by furnace and high-pressure burner rig exposures. Although protective SiO₂ scales formed in all cases, the evidence presented supports a model based on parabolic growth kinetics (i.e., parabolic growth moderated simultaneously by linear volatilization). The volatility rate is dependent on temperature, moisture content, system pressure, and gas velocity. The burner tests were thus used to map SiO₂ volatility (and SiC recession) over a range of temperatures, pressures, and velocities. The functional dependency of material recession (volatility) that emerged followed the form $A[\exp(-Q/RT)](P^x v^y)$. These empirical relations were compared with rates predicted from the thermodynamics of volatile SiO and SiO_xH_y reaction products and a kinetic model of diffusion through a moving boundary layer. For typical combustion conditions, recession of 0.2 to 2 μm/hr is predicted at 1200 to 1400 °C, far in excess of acceptable long-term limits.

Introduction

Silicon carbide composites have been proposed as liner material for advanced combustors in turbine engines. Here the operational pressures are about 10 atm. Conventional (lean) operation produces a combustion product consisting of

10% O₂–8% H₂O–7% CO₂–bal. N₂ at an equivalence ratio ϕ of 0.5 (ref. 1). Other combustor concepts use a rich-burn prechamber in which a hyperstoichiometric mixture of fuel to air (ϕ of about 1.5) is burned with a projected combustion chemistry of 6% H₂–12% H₂O–12% CO–5% CO₂–bal. N₂. The rich-burn segment is followed by a quick air-quench and lean aft-burn segment. Volatile reaction products between the SiO₂ scales and the combustion gases have been a concern of this program. It was shown in allied furnace thermogravimetric analysis (TGA) exposures that Si(OH)₄(g) and SiO(g) are produced when SiC is exposed to model lean and rich gases, respectively (refs. 2, 3, and D.S. Fox, E.J. Opila, and R.E. Hann, 1999, unpublished data). Although a scale is first produced by oxidation, it then reacts with the gas to form a volatile secondary product. This reaction gives rise to parabolic kinetics and accelerated consumption of the substrate (recession) (ref. 2), which represents a nonprotective oxidation regime. Consequently, long-term exposures are predicted to produce linear attack rates. These rates are determined by the thermodynamics of the equilibrium vapor species, the ambient pressure, and the gas velocity. Although a number of burner rig studies have been performed on SiC (ref. 4), only one has recently combined the use of high pressure and high velocity to clearly produce weight loss (ref. 5). No previous studies have addressed the effect of rich-burn combustion.

The purpose of the present study was to examine the behavior of pure, chemical vapor-deposited (CVD) SiC under a variety of high temperatures, pressures, and velocities for both lean-burn and rich-burn combustion. The study was conducted in a high-pressure burner rig (HPBR). Some experimental

results are presented in greater detail in previous reports (refs. 6 and 7), and chemical mechanisms are covered in greater depth in reference 8. The volatility rates in HPBR tests are compared with those measured in the furnace TGA tests and those calculated from the thermodynamic diffusion model. For comparison, recession rates were also obtained on CVD and sintered Si_3N_4 materials.

Experiment

High-purity CVD SiC and Si_3N_4 materials (Bomas Machine Specialties and Advanced Ceramics Corp.) were machined to 0.3- by 1.3- by 2.5-cm TGA specimens or to 0.3- by 1.3- by 7.6-cm HPBR specimens. Thermogravimetric analysis tests were performed with Cahn 1000 microbalances and furnaces using quartz tubes. Model lean exposures employed a 50-percent $\text{H}_2\text{O}/\text{O}_2$ mixture to approach the high water vapor pressure of a combustor (ref. 2). This mixture is compared with a moisture content of 8 percent \times 10 atm, or 80 percent, which would be more representative of the actual combustor conditions. A special double-chamber water saturator, followed by tape-heated gas lines, was employed to insure accurate control of the moisture content. The gas flow was 4.4 cm/s. Model rich exposures were made in a premixed gas flowing through a similar saturator to give 4% H_2 -12% H_2O -10% CO -7% CO_2 - N_2 flowing at 0.44 cm/s (D.S. Fox, E.J. Opila, and R.E. Hann, 1999, unpublished data).

An existing high-pressure burner rig was extensively modified to allow lean-burn and rich-burn testing of multiple ceramic specimens (fig. 1). References 6 and 7 give details of the rig construction and operation. The basic operation entails pressurized fuel and air injection (in an air blast nozzle and swirl plate dome section), ignition (by hydrogen gas at a spark plug), and combustion product formation (in an air-cooled, thermal-barrier-coated combustor can). The gaseous combustion products proceed through a water-cooled transition section and lose heat in the process. Specimens are arranged in a wedge configuration in a water-cooled specimen holder, pneumatically actuated into or out of the flowing gas. The gas temperature is measured by a Pt-Pt13Rh thermocouple at a position just behind the samples. The sample temperature is measured by two-color optical and laser pyrometry (lean-burn only). The luminous flame produced under rich conditions precluded measurements by optical pyrometry. Therefore, rich-burn temperatures were determined from thermocouple measurements of gas temperature and a specimen temperature calibration curve produced from lean conditions.

The intention was to determine volatility rates over a range of temperatures, pressures, and velocities. To that end, some flexibility in operational parameters existed; however, an interdependence between variables resulted in certain restrictions. Nominal fuel-lean combustion at $\phi = 0.8$ to 0.9 and fuel-rich combustion at $\phi = 1.8$ to 2.0 produced sample temperatures from 1200 to 1450 °C. Standard operating pressure and velocity were 6 atm and 18 to 25 m/s, respectively. For selected tests, the pressure was also varied from 4 to 15 atm whereas velocity for the most part was a dependent variable.

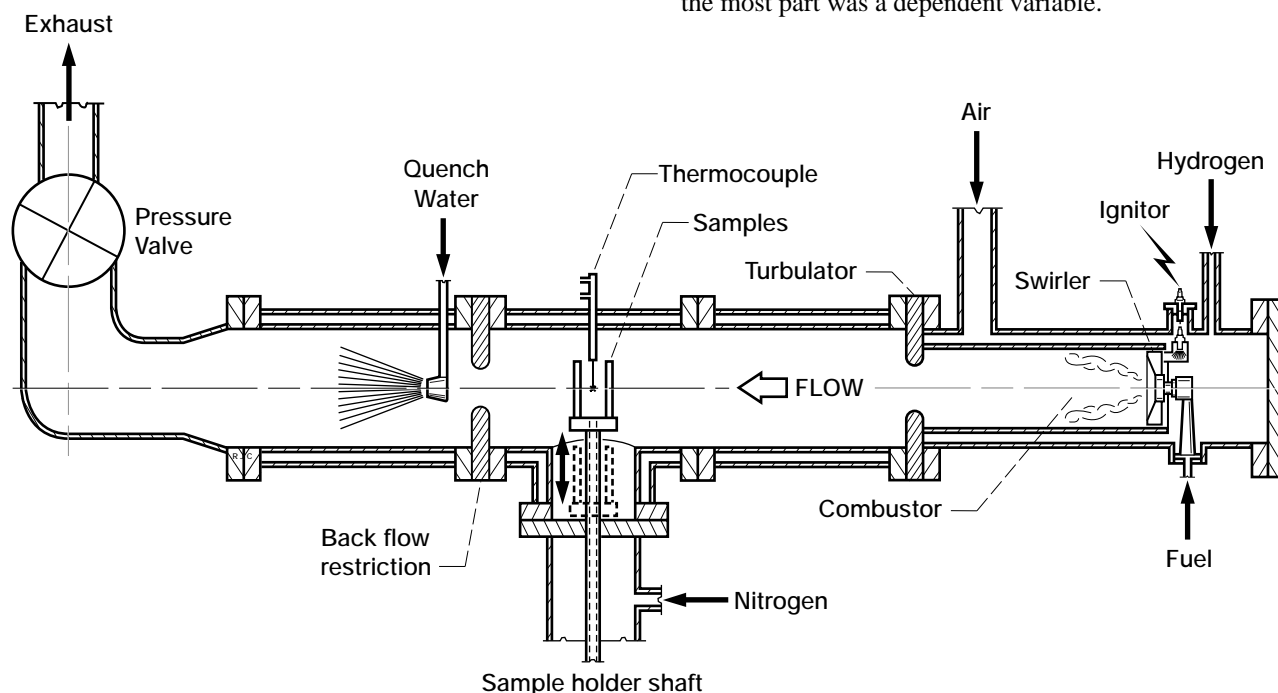


Figure 1.—NASA Glenn high-pressure burner rig (HPBR).

Results

Furnace Tests

In model lean furnace tests, mixtures of 10 percent $\text{H}_2\text{O}/\text{O}_2$ failed to produce appreciable differences in kinetics from tests performed in dry O_2 environments. However, at 50 percent $\text{H}_2\text{O}/\text{O}_2$, which would be more representative of a moist environment at high pressures, a negative (paralinear) deviation from parabolic kinetics was observed. An analysis of weight change data yielded a parabolic growth constant k_p and a linear recession rate k_l (ref. 2). A typical curve and fitted parameters for CVD SiC oxidized in 50 percent $\text{H}_2\text{O}/\text{O}_2$ (lean) at 1200 °C are given in figure 2. The actual (sawtooth) data and fitted net weight change (smooth) curves are coincident and provide a high degree of confidence for the mathematical model. The model weight gain curve is indicative of the amount of scale present on the sample, whereas the model weight loss curve indicates the amount of Si (and C) lost during oxidation and SiO_2 scale volatilization. There was only a slight temperature dependence of k_p and k_l in lean furnace tests with water vapor (refs. 2 and 9).

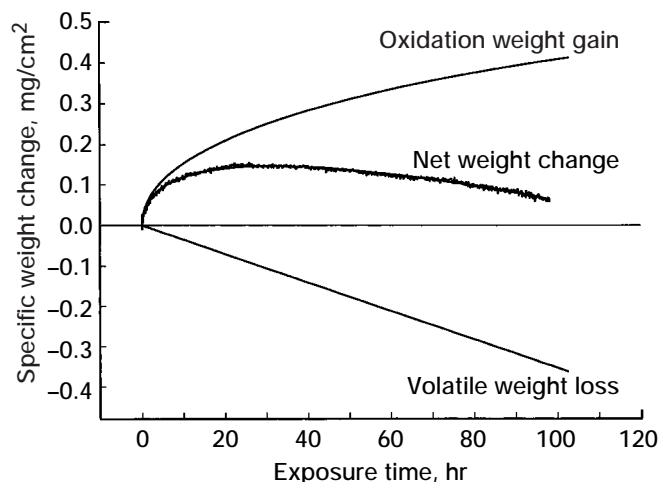


Figure 2.—Paralinear weight change curves for CVD SiC in synthetic 50-percent $\text{H}_2\text{O}/\text{O}_2$ (lean) furnace TGA environment at 1200 °C. Parabolic growth constant, k_p , $2.7 \times 10^{-3} \text{ mg}^2/\text{cm}^4 \cdot \text{hr}$; linear recession rate, k_l , $5.3 \times 10^{-3} \text{ mg}/\text{cm}^2 \cdot \text{hr}$.

A strong temperature dependence of SiC recession due to SiO_2 volatility was produced in synthetic rich gas mixtures, as shown in the composite TGA curves of figure 3. Here, very little volatility could be detected below 1350 °C using the same paralinear model and data analysis (D.S. Fox, E.J. Opila, and R.E. Hann, 1999, unpublished data). However, at 1400 °C and above, the volatility rates were appreciable.

A comparison of the SiC weight loss rates in lean and rich furnace test environments is presented in the Arrhenius plot of figure 4. A higher temperature dependency is observed for rich environments. It should be noted that the fuel-rich tests were performed at one-tenth the gas flow of the fuel-lean exposures. Also, x-ray diffraction and scanning electron microscopy (SEM) confirmed that a continuous cristobalite scale was present under all furnace exposures and that active oxidation was not responsible for these weight losses.

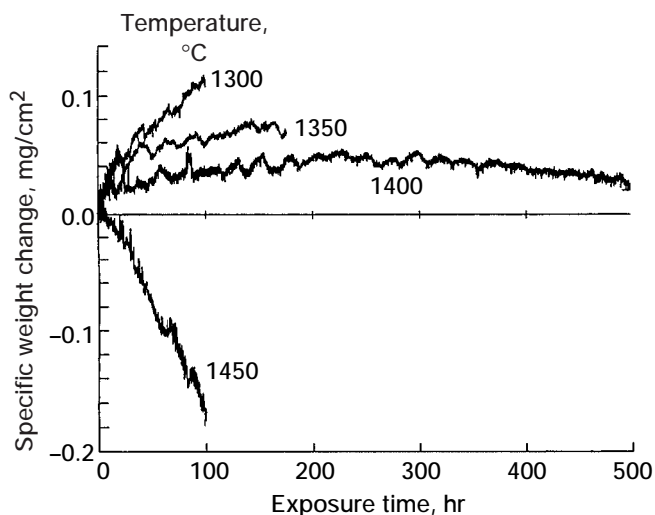


Figure 3.—Temperature dependence of weight change behavior of CVD SiC in synthetic fuel-rich TGA furnace environments (4% H_2 -12% H_2O -10% CO -7% CO_2 - N_2).

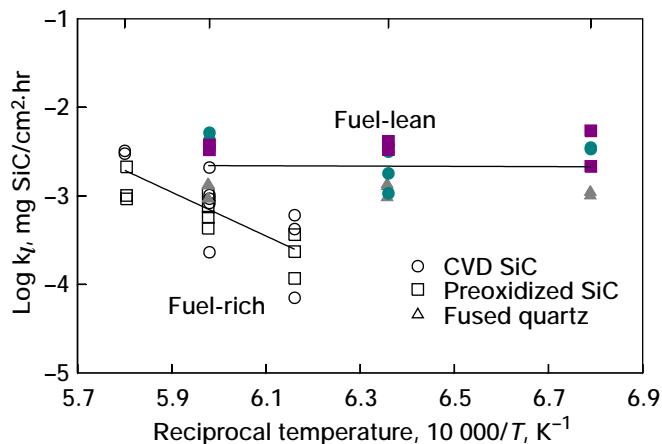


Figure 4.—Comparative Arrhenius plots of SiC loss rates for synthetic fuel-lean and fuel-rich TGA furnace environments.

Burner Rig Tests

In HPBR testing, linear weight loss rates were also observed, although the initial interval of weight gains characteristic of parabolic oxidation was generally not observable. Selected test results are shown in figure 5 for CVD SiC tested under fuel-lean conditions. Linear rates of thickness loss were also observed and showed similar temperature dependencies (ref. 7). The correlation between SiC thickness and weight loss, calculated from the density of SiC (3.2 g/cm^3), is $3.1 \mu\text{m}$ for each milligram per square centimeter of SiC consumed. Accordingly, a factor of 2.9 was measured experimentally and demonstrated that weight loss is also a reliable indicator of surface recession.

More than 30 test runs at 6 atm yielded the two corresponding Arrhenius curves in figure 6. In comparison with lean combustion, a somewhat higher absolute recession rate and activation energy are indicated for rich combustion. Sintered SiC (Hexoloy) and several composite samples (DuPont SiC/SiC, enhanced SiC/SiC, Supertemp, and RT 42 coatings) all exhibited weight loss behavior basically equivalent to that of CVD SiC under the same range of test conditions.

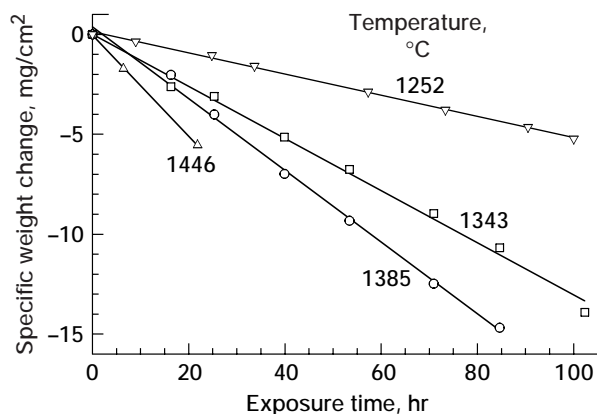


Figure 5.—Effect of sample temperature on linear rate of SiC weight loss under fuel-rich HPBR combustion. Pressure, P , 6 atm; velocity, v , 18 to 20 m/s.

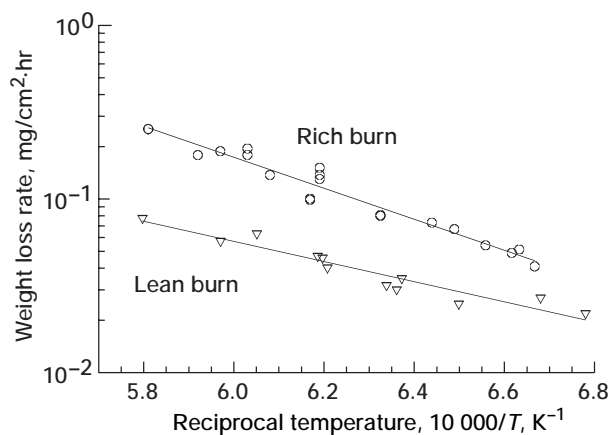


Figure 6.—Comparative Arrhenius plots of SiC recession rates under fuel-rich and fuel-lean HPBR combustion. Pressure, P , 6 atm; velocity, v , 18 to 20 m/s.

Similar experiments were performed on CVD and sintered (AS 800) Si_3N_4 under fuel-lean conditions. The weight change curves in figure 7 show immediate linear loss rates for the CVD material but show parabolic behavior for the sintered Si_3N_4 . Parabolic behavior (i.e., initial weight gains before approaching a linear weight loss rate) was reported for furnace tests of SiC and Si_3N_4 in water vapor (refs. 2, 9, and 10). The temperature dependency of Si_3N_4 recession rates exhibits activation energies similar to those for SiC in the Arrhenius plot of figure 8. However, the absolute value of the rate is 1.8 times that of SiC. In synthetic (50 percent $\text{H}_2\text{O}/\text{O}_2$) fuel-lean furnace TGA tests, the same materials exhibited volatility rates nearly equal to those of SiC (ref. 10). At this time there is no plausible explanation for these differences.

Another series of tests determined that increased pressure resulted in increased volatility rates (ref. 7). However, an absolute relationship cannot be directly claimed because of the simultaneous decrease in velocity. Pressure effects will therefore be discussed after the general volatility model is presented.

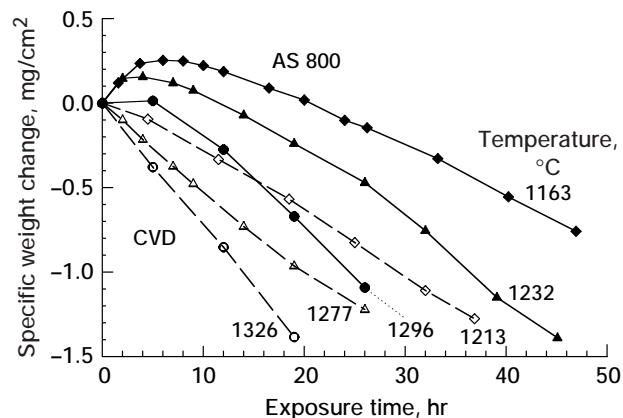


Figure 7.—Linear and parabolic oxidation curves for CVD and sintered (AS 800) Si_3N_4 under lean-burn combustion. Pressure, P , 6 atm; velocity, v , 21 to 23 m/s.

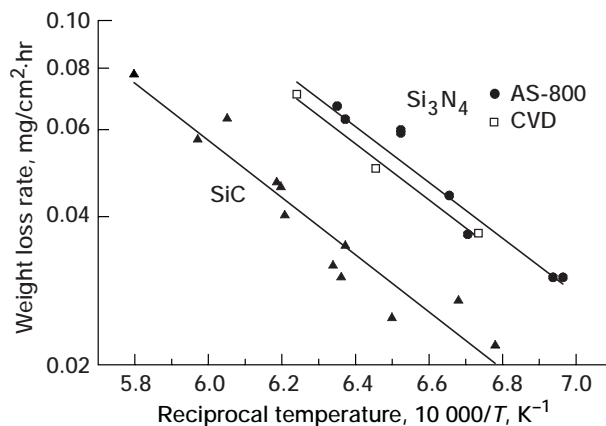


Figure 8.—Comparative Arrhenius plots of SiC and Si_3N_4 lean-burn recession rates. Activation energy, Q , for SiC, 111 kJ/mole-K and for Si_3N_4 , 108 kJ/mole-K

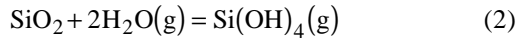
Discussion

Volatility Rate Model

The general temperature dependence derives from the equilibrium constants of pertinent reactions:

$$\Delta G_o = -RT \ln K_{eq} \quad (1)$$

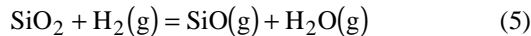
For example, the reaction of SiO_2 ($a = 1$) with water vapor has an equilibrium vapor pressure of Si(OH)_4 given by



$$K_{eq} = \frac{P_{\text{Si(OH)}_4}}{\left(a_{\text{SiO}_2} \cdot P_{\text{H}_2\text{O}}^2\right)} \quad (3)$$

$$P_{\text{Si(OH)}_4} = \exp\left(\frac{-\Delta G_o}{RT}\right) \cdot P_{\text{H}_2\text{O}}^2 \quad (4)$$

or for a possible rich-burn reaction,



$$K_{eq} = \frac{(P_{\text{SiO}} \cdot P_{\text{H}_2\text{O}})}{\left(a_{\text{SiO}_2} \cdot P_{\text{H}_2}\right)} \quad (6)$$

$$P_{\text{SiO}} = \exp\left(\frac{-\Delta G_o}{RT}\right) \cdot \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} \quad (7)$$

A model of SiO_2 volatilization was developed in detail in references 2 and 8 and is illustrated in the schematic of figure 9. In short, material removal was approximated by the diffusion of a volatile species (shaded spheres) through a boundary layer moving with laminar flow across the reactant surface. Ideally, velocity varies across the boundary layer from zero at the sample surface to the free-stream velocity at the boundary edge (vectors). The equation describing such a flux is given by (ref. 2):

$$J = 0.664(\text{Re})^{1/2}(\text{Sc})^{1/3}\left(\frac{D\rho v}{L}\right) \quad (8)$$

or equivalently,

$$J = 0.664\left(\frac{\rho'vL}{h}\right)^{1/2}\left(\frac{h}{\rho'D}\right)^{1/3}\left(\frac{D\rho}{L}\right) \quad (8a)$$

where Re is the Reynolds number, Sc is the Schmidt number, D is the interdiffusion coefficient for the volatile species in the combustion gas, ρ is the concentration of the volatile species at the solid-gas interface, v is the linear gas velocity, L is the characteristic sample length parallel to the flow and over which the volatility is averaged, ρ' is the concentration of the major gas component, and h is the gas viscosity. Other details required for the calculation are described in references 2 and 8. The objective herein is to illustrate the origins of the terms required to represent a simple functional relationship between recession rate and temperature, pressure, and velocity.

The net result of the factors in equations (4), (7), and (8) on the flux of Si(OH)_4 and SiO volatile products is given by equations (9) and (10), respectively:

$$J_{\text{Si(OH)}_4} \propto \left[\exp\left(\frac{-\Delta G_o}{RT}\right)\right] v^{1/2} \left(\frac{P_{\text{H}_2\text{O}}^2}{P_{\text{total}}^{1/2}}\right) \quad (9)$$

$$J_{\text{SiO}} \propto \left[\exp\left(\frac{-\Delta G_o}{RT}\right)\right] v^{1/2} \left(\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}} \cdot P_{\text{total}}^{1/2}}\right) \quad (10)$$

Given that the pressure of the reactants varies directly with the total system pressure, the functional forms can be further simplified:

$$J_{\text{Si(OH)}_4} \propto \left[\exp\left(\frac{-\Delta G_o}{RT}\right)\right] v^{1/2} (P_{\text{total}}^{3/2}) \quad (9a)$$

$$J_{\text{SiO}} \propto \left[\exp\left(\frac{-\Delta G_o}{RT}\right)\right] v^{1/2} (P_{\text{total}}^{-1/2}) \quad (10a)$$

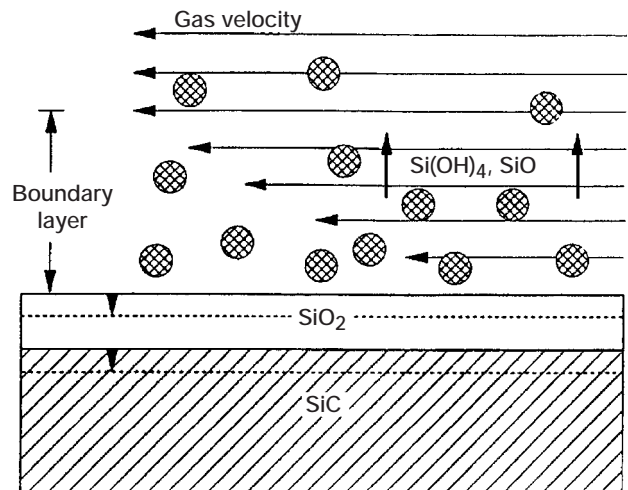


Figure 9.—Model of physical SiO_2 scale volatility process (gaseous diffusion through a moving boundary layer) and corresponding SiC recession.

Comparison With Measured Data

A general parametric dependency according to $\left[\exp(-Q/RT)\right](P^x v^y)$ can thus be expected for recession rates. From the appropriate thermodynamics and flow conditions, the vapor species flux was calculated for a low-velocity, 1-atm furnace (fig. 10) and for a high-velocity, 6-atm burner rig (fig. 11), and the results were compared with experimental data. For lean exposures, good agreement exists for the measured and calculated values if an $\text{Si}(\text{OH})_4$ gaseous reaction product (fig. 10) is assumed.

For rich exposures, good agreement was found for the furnace tests if an SiO vapor species was assumed (fig. 11). However, the higher pressures of the burner rig tests resulted in the predicted vapor pressure and contribution of this species being minor. The potential contribution of the $\text{Si}(\text{OH})_4$ species is shown, but the lack of agreement suggests that other species may be controlling. Although $\text{SiO}(\text{OH})_2$ and $\text{Si}_2(\text{OH})_6$ molecules have been considered, the available thermodynamic data do not yet support any single species (ref. 8).

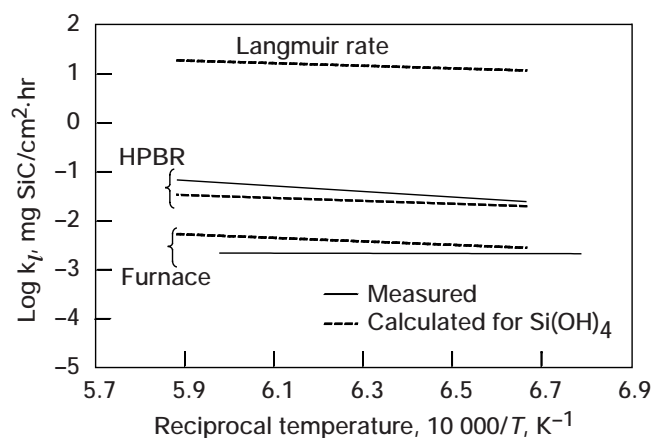


Figure 10.—Comparison of calculated and measured SiC recession rates under fuel-lean conditions.

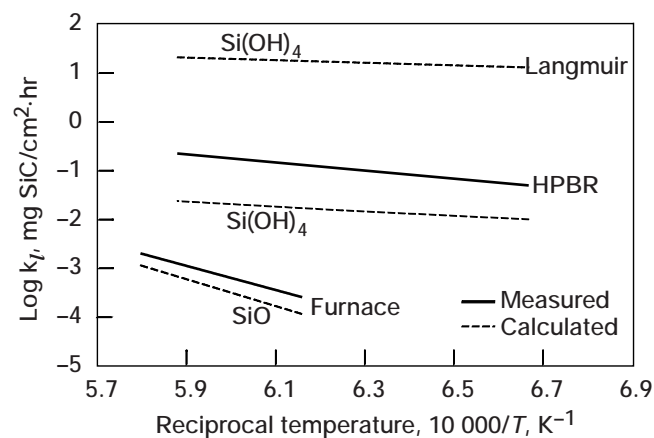


Figure 11.—Comparison of calculated and measured SiC recession rates under fuel-rich conditions.

Figures 10 and 11 also show the Langmuir rates as an upper bound to what would be predicted if there were no gaseous boundary layer diffusion control or to what would be approached as the flow exceeded turbulent conditions:

$$J_{\text{Langmuir}} = P_{\text{species}} \left(\frac{M_{\text{species}}}{2\pi RT} \right)^{1/2} \quad (11)$$

where P is the equilibrium vapor pressure and M is the molecular weight of the volatile species. The Langmuir rates are at least 2 orders of magnitude greater than those produced by HPBR exposures. Thus, the volatility rates measured in burner rig tests more nearly approach those calculated from the boundary layer equation, even though ideal laminar flow was not expected in these tests.

Normalized Recession Rates

A second series of HPBR experiments was performed to illustrate the effects of pressure and velocity. The twofold purpose was to verify the diffusional model and to provide key information (Q and x) regarding the controlling chemical mechanism. Velocity and pressure were interdependent variables in the high-pressure burner rig; therefore, the data were displayed in figure 12 according to a combined variable (i.e., normalized with respect to the factor $P^{3/2} v^{1/2}$). The results show that rich and lean exposures produce recession rates that conform reasonably well to a boundary layer diffusion model with a $P^{3/2}$ pressure dependency, where again the rich-burn rates and activation energy were higher. More precisely, a multiple linear regression analysis of lean and rich data sets, containing 24 and 34 points, respectively, yielded the following fits to the data (ref. 7). For lean,

$$k_f (\text{mg} / \text{cm}^2 \cdot \text{hr}) = 2.04 \exp \left(\frac{-108 \text{ kJ} / \text{mole} \cdot \text{k}}{RT} \right) P^{1.50} v^{0.50} \quad (12)$$

and the correlation coefficient $R^2 = 0.98$.

For rich,

$$k_f (\text{mg} / \text{cm}^2 \cdot \text{hr}) = 82.5 \exp \left(\frac{-159 \text{ kJ} / \text{mole} \cdot \text{k}}{RT} \right) P^{1.74} v^{0.69} \quad (13)$$

and $R^2 = 0.95$.

where the linear recession rate is in milligrams per square centimeter per hour, the pressure is in atmospheres, the velocity is in meters per second, and temperature is in Kelvin.

The lean relationship is thus in exceptional agreement with the predicted $P^{3/2} v^{1/2}$ boundary layer analysis, which includes the pressure dependency for the $\text{Si}(\text{OH})_4$ molecule. The rich

relationship is less clear, exhibiting a nonideal velocity exponent and a pressure dependency somewhat higher than $3/2$, in disagreement with the proposed $P^{-1/2}$ relationship for SiO formation. In any event, these empirical equations can be used to predict recession for a variety of conditions. Examples of lean-burn and rich-burn recession under some generic combustor conditions are presented in table I. Clearly, high values are obtained at temperatures equal to or greater than 1200 °C. High rates would also be expected for turbine airfoils because of the higher pressures and velocities associated with this stage.

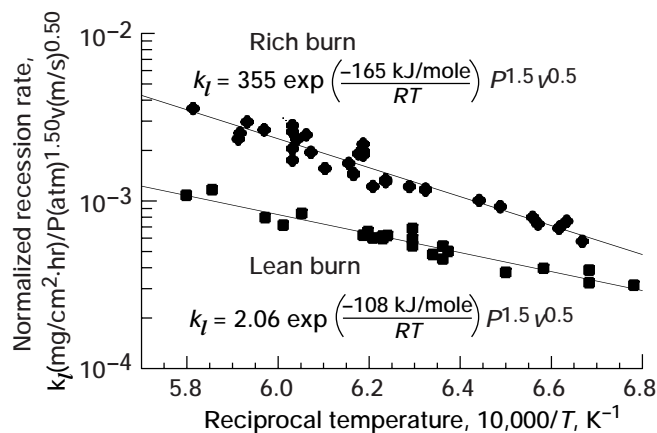


Figure 12.—Universal SiC recession rates in HPBR tests, normalized for all pressures and velocities by the factor $P^{3/2} v^{1/2}$.

TABLE I.—PROJECTED SiC RECESSION FOR VARIOUS TEMPERATURES UNDER GENERIC COMBUSTOR CONDITIONS

Temperature, <i>T</i> , °C	[Pressure, 10 atm.]	
	Lean burn (velocity, 90 m/s)	Rich burn (velocity, 30 m/s)
	Recession rate, <i>k_f</i> , μm/1000 hr	
1000	70	40
1100	140	130
1200	270	330
1300	480	760
1400	790	1580
1500	1230	3010

Conclusions

The oxidation behavior of chemical vapor-deposited (CVD) and sintered SiC and Si₃N₄ materials was evaluated under synthetic furnace and actual high-pressure burner rig fuel-lean and fuel-rich combustor conditions. All tests yielded weight loss rates indicative of gaseous reaction products. The furnace test rates agreed with model calculations based on Si(OH)₄ (fuel-lean) or SiO (fuel-rich) volatile species. The high-pressure burner rig tests yielded pressure and velocity dependencies that also suggested volatilization phenomena. Good regression fits to the recession rates were obtained for the functional form $A[\exp(-Q/RT)](P^x v^y)$. Recession was higher in the fuel-rich rig test than in the fuel-lean rig test, but both will result in significant recession after long-term exposures. The critical fuel-lean species appeared to be Si(OH)₄ in the furnace and burner rig but is known to be SiO only for the fuel-rich furnace (atmospheric) condition. The Si₃N₄ materials also exhibited scale volatility in the fuel-lean furnace and rig tests.

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National Aeronautics and Space Administration
Cleveland, Ohio, April 12, 1999

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